

Supplementary Information

Scaling resistance by fluoro-treatments: The importance of wetting states

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Supplementary Information includes:

S1: Preparation of PDMS elastomer

Briefly, a specific amount of PDMS mixture, with the weight composition of PDMS and the curing agent being 10:1, was spread onto the silicon wafer. Afterwards, the mixture was placed in an oven at 60 °C for 3 h to allow simultaneous curing and moulding. The as-obtained PDMS elastomer was peeled off and used as a substrate for the casting process.

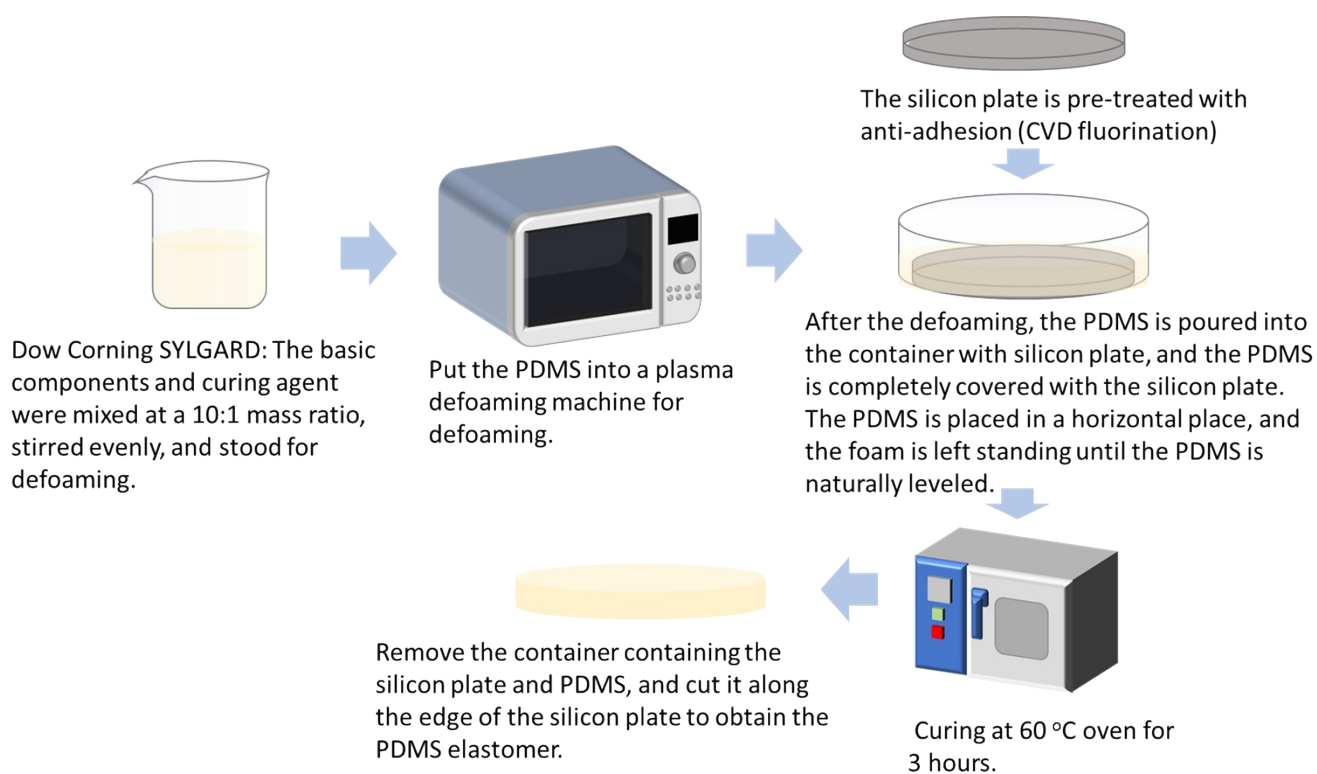


Fig. S1 Preparation schematic diagram of PDMS elastomer.

S2: Calculation of surface energy

Surface energies of pristine and 17-FAS, CF₄ modified membrane substrates were estimated using the LW/AB method (Eq.1) based on independent contact angles with three different liquids [1]. The contact angles were measured by a contact angle goniometer (Maist Drop Meter A-100P) via the sessile drop method, as shown in section 2.4 in the main texts.

$$(\gamma_L^{LW} + 2\sqrt{\gamma_L^+ \gamma_L^-})(1 + \cos\theta) = 2(\sqrt{\gamma_S^{LW} \gamma_L^{LW}} + \sqrt{\gamma_S^+ \gamma_L^-} + \sqrt{\gamma_S^- \gamma_L^+}) \quad (1)$$

Table S1 Contact angles of three membranes

	MP-PVDF	FAS-MP-PVDF	CF4-MP-OVDF
Water/°	155.3±1.7	164.1±3.9	166.2±1.5
Diiodomethane	63.5±4.0	156.3±7.8	155.0±4.1
glycerol	144.4±5.0	156.0±3.8	151.7±5.5

Table S2 Surface free energy parameters of test liquids $\gamma/(mJ.m^{-2})$

	γ_L	γ_L^{LW}	γ_L^+	γ_L^-
water	72.8	21.8	25.5	25.5
Diiodomethane	50.8	50.8	0	0
glycerol	64.0	34.0	3.92	57.4

The surface energy parameters of the solid can be obtained by measuring the contact angle between the solid surface and the three liquids with known γ_L^{LW} , γ_L^+ , γ_L^- values.

Table S3 Surface energies of three membranes determined by the LW/AB method

	MP-PVDF	FAS-MP-PVDF	CF4-MP-PVDF
Surface energy/ $\text{mJ}\cdot\text{m}^{-2}$	33.72 \pm 3.10	0.16 \pm 0.15	0.46 \pm 0.25

S3: Results of measurements and calculation process for slip length

The slip length of the membrane was determined by torque measurement using a rheometer (AR-2000ex). A thermostatic controlled Peltier plate (base plate) was maintained at a constant temperature of 25 ± 0.2 °C. The membrane samples were carefully fixed to the base plate via tape, a stainless-steel cone plate with a diameter of 50 mm and cone angle of 1° was used to measure liquid viscosity on membranes, whose shear rate range was set at 30-100 (s^{-1}). The equipment was pre-calibrated using deionised water: deionised water and 20 wt.% glycerin solutions were chosen as the test liquids.

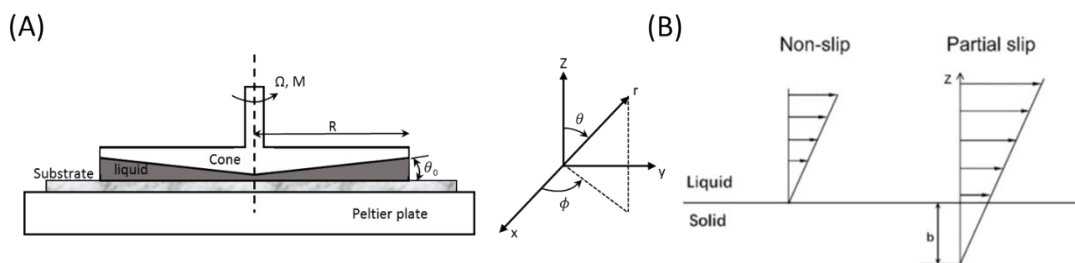


Fig.S2 (A) Schematic drawing of a cone-and-plate rheometer. (B) Schematic of non-slip and slip boundary conditions.

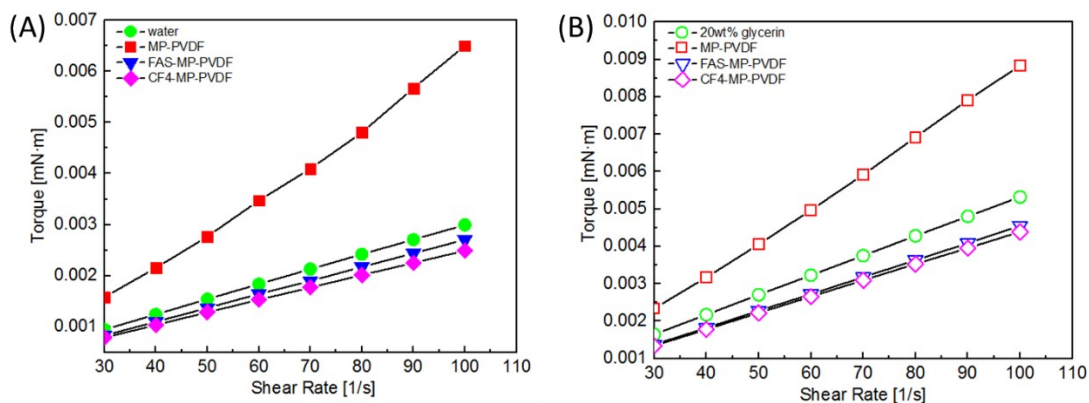


Fig. S3 Torque of MP-PVDF, FAS-MP-PVDF, CF4-MP-PVDF membranes corresponding to shear rates varying from 30 1/s to 100 1/s. (A) corresponds to deionised water as the test liquid, and (B) corresponds to 20 wt.% glycerin.

Slip length of three membranes was determined with eq.2 [2]:

$$M = \int_0^R 2\pi r^2 \tau_{\theta\phi} dr = \frac{2\pi\mu\Omega R^3}{3\theta_0} \left(1 - \frac{3\delta}{2R\theta_0} + \frac{3\delta^2}{R^2\theta_0^2}\right) \quad (2)$$

Where M is the torque, μ is the viscosity of the test liquid, Ω is the angular velocity, R is the radius of the cone plate, θ_0 is the cone Angle, $\tau_{\theta\phi}$ is the shear stress in the direction of ϕ , and δ is the slip length. The calculated slip lengths are shown in Fig.7 of the main text.

S4: Surface roughness of the membranes.

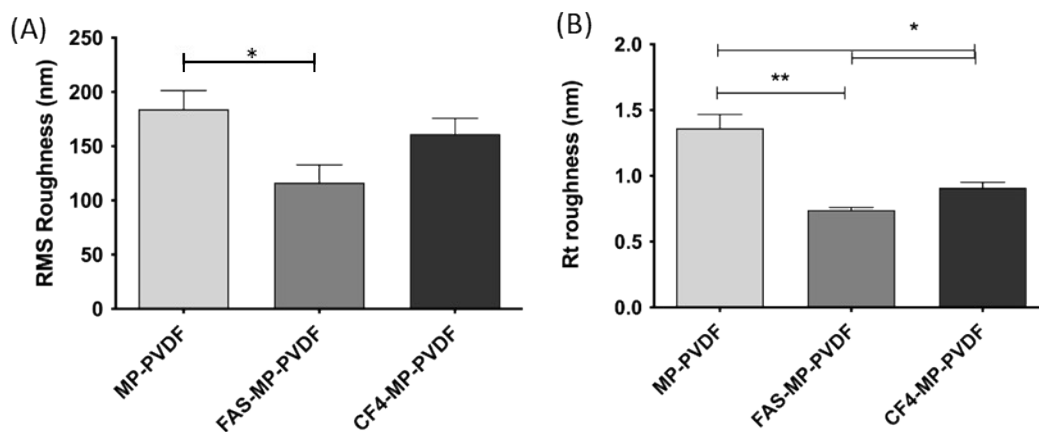


Fig. S4 The effects of CF₄ Plasma or fluorosilane treatment on surface morphology. (A) The root means square roughness (RMS) and (B) The Peak-to-valley roughness (Rt) of MP-PVDF, FAS-MP-PVDF, CF₄-MP-PVDF. Roughness values were obtained from a scan size of 3 μm x 3 μm on the top surface of micropillars. * indicates p<0.05 and thus there is a significant difference.

S5: Physical significance of parameter in the wetting state factor calculation formula

The wetting state of the surface with pillar structure was identified using the wetting state factor ζ [3], defined as:

$$\zeta = \frac{(\sqrt{2}S_f - 1)}{2a_r} \tan(\theta_a - \varphi) \quad (3)$$

Where S_f indicates the spacing factor (ratio of pitch to diameter), a_r is aspect ratio given by height and diameter of pillar on the membrane, θ_a is advancing angle and φ is the interior angle as a geometrical factor ($\varphi=90^\circ$ for cylindrical pillars).

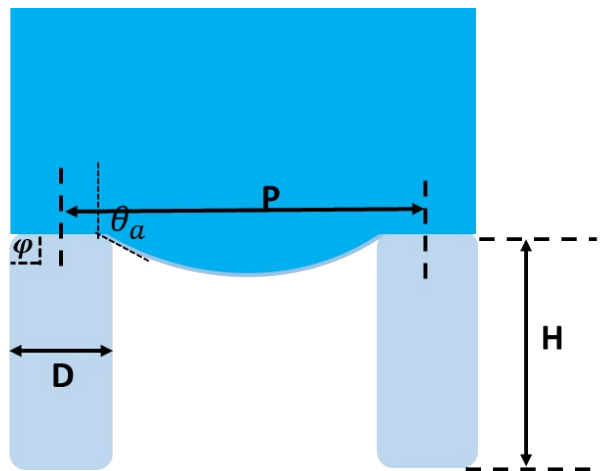


Fig. S5 Physical significance of parameters involved in the calculation of the wetting state factor.

spacing factor $S_f = P/D$, aspect ratio $a_r = H/D$, $P=10 \mu\text{m}$, $D=5 \mu\text{m}$, $H=10 \mu\text{m}$.

S6: The curve of actual flux for three membranes

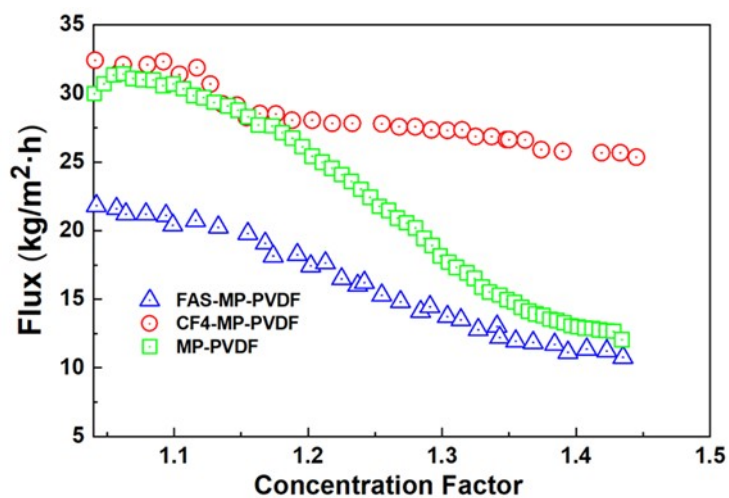


Fig. S6 The actual flux as a function of concentration factor. The initial flux of MP-PVDF, FAS-MP-PVDF and CF4-MP-PVDF was 31.2 kg/m²·h, 21.6 kg/m²·h, 32.1 kg/m²·h, respectively.

References:

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